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## JAPANESE PATENT OFFICE

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(71)Applicant:

NIPPON ZEON CO LTD

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(72)Inventor:

IZAWA YUTAKA  
AOKI MITSURU  
KASAI JUNJI

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(54) MULTILAYER COATED PAPER FOR WEB ROTARY OFFSET PRESS

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a multilayer coated paper for web rotary offset press that has excellent balance between dry strength, white paper gloss, multicolor printing gloss and blistering resistance.

SOLUTION: In a at least 2 coating layers-having multilayer coated paper for web rotary offset press, a coating layer including hemispheric particles formed from a coating composition that comprises 100 pts.wt. of a pigment, 40 pts.wt. of a binder and 0.3-10 pts.wt. of hollow or hemispheric polymer particles, or their precursor particles.

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CLAIMS

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[Claim(s)]

[Claim 1] The multilayer coated paper for offset rotation printing which is a multilayer coated paper for offset rotation printing which has at least two or more layers of the coating layers which make a pigment and adhesives a principal component, and is characterized by a top coating layer containing an empty capsid or bowl type polymer grain.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the multilayer coated paper for offset rotation printing. Furthermore, it is related with the multilayer coated paper which has the blister-proof nature which was excellent in optical properties, such as a surface intensity, and blank paper gloss, printing gloss, and was further especially excellent in offset rotation printing intended use in detail.

[0002]

[Description of the Prior Art] In recent years, it is asked for the coated paper which the performance required of a coated paper is also severe in connection with rapid development of offset rotation printing technique, for example, satisfies simultaneously both the properties of a bond strength and blister-proof nature. However, both this property is usually in the relation of a trade-off. That is, if one property is raised, the property of another side will fall. In offset rotation printing, it is required to dry the printed ink momentarily and xeransis is performed in an elevated temperature and a high-speed dryer. Therefore, although the moisture contained in a coated paper serves as a steam momentarily, if this steam is not emitted outside at an instant, a blister phenomenon occurs and it is valueless as a coated paper. Although there is also the technique of raising the paper intensity of coating stencil paper to the level which is not destroyed by the water vapor pressure in order not to generate a blister phenomenon, as the steam permeability of a coating layer is raised and the generated steam is usually easily discharged out of paper, the technique of a high water vapor pressure being made not to produce in paper is adopted.

[0003] In order to form such a coating layer, many things for which a specific thing is used for the synthetic-macromolecule latex used as the adhesives component, especially the main adhesives in a coating constituent are mainly proposed until now. Such technique uses what has a gel content few as a latex. However, when such a latex is used, although blister-proof nature is improved, the surface intensity of a coated paper may fall on the other hand, it may cause the problem of a pie ring or blanket dirt in high-speed printing, and also a printability like printing gloss is inferior in it.

[0004] Moreover, the method of preparing the layer containing a specific empty capsid is indicated by JP,6-280194,A as a layer in contact with stencil paper. However, according to the study of this invention persons, there is a point that some should be improved in this technique. That is, in order to acquire the blister-proof nature enhancement effect which may be satisfied, a lot of empty capsids need to be used. Since the coating liquid concentration of an under coat is not fully raised by this technique, there is a problem on operation of Myst occurring. Moreover, since it is necessary to evaporate more moisture, when big xeransis energy is needed and xeransis on a process is not fully performed, the moisture regain of a coated paper goes up and the coated paper with good blister-proof nature is not obtained. Moreover, in order that the smooth nature on the front face of an under coat might go up too much, a certain thing also made clear the problem that the high-speed coating fitness at the time of finishing was not enough.

[0005]

[Problem(s) to be Solved by the Invention] Therefore, it is in the purpose of this invention offering the

multilayer coated paper for offset rotation printing which was excellent in blister-proof nature, and was excellent in a surface intensity, blank paper gloss, and printing gloss.

[0006]

[Means for Solving the Problem] When forming the top coating layer using the coating constituent containing an empty capsid or bowl type polymer grain as a result of repeating a research zealously in order to attain the above-mentioned technical problem, this invention persons find out that blister-proof nature is improvable, and came to complete this invention based on this knowledge.

[0007] In this way, according to this invention, it is the multilayer coated paper for offset rotation printing which has at least two or more layers of the coating layers which make a pigment and adhesives a principal component, and the multilayer coated paper for offset rotation printing characterized by a top coating layer containing an empty capsid or bowl type polymer grain is offered.

[0008]

[Embodiments of the Invention] Although the multilayer coated paper of this invention has a two or more-layer coating layer, it requires that the top coating layer (it may be hereafter called a top layer) which is the maximum surface layer of a multilayer coated paper should contain an empty capsid or bowl type polymer grain.

[0009] Although it will not be limited especially if the empty capsid which can be used for this invention is an organic empty capsid, what uses thermoplastic resin as husks from the point of blister-proof nature enhancement is desirable. It is also possible to use such an inorganic empty capsid together to an organic empty capsid as an empty capsid, in the domain by which the effect of this invention is not spoiled, although the thing of the minerals like a ceramic balloon is also known.

[0010] As an empty capsid which uses thermoplastic resin as husks, polystyrene, the Poly alpha methyl styrene, Styrene resins and polymethyl methacrylates, such as a Poly beta-methyl styrene, A polymethacrylic-acid ethyl, a polymethacrylic-acid isopropyl, a polymethacrylic-acid isobutyl, Others [ resins / acrylic /, such as a polyacrylonitrile and a poly-methacrylonitrile ], A polyvinyl chloride, a polytetrafluoroethylene, polyvinyl alcohol, Poly o-vinyl benzyl alcohol, Poly m-vinyl benzyl alcohol, Poly p-vinyl benzyl alcohol, a polyvinyl formal, a polyvinyl acetal, Polyvinyl pro \*\*\*\*\*, a polyvinyl butyral, a polyvinyl iso butyral; Various kinds of things, such as a polyvinyl tertiary butyl ether, a polyvinyl pyrrolidone, a polyvinyl carbazole, cellulose acetate, a cellulose triacetate, and a polycarbonate, can be illustrated. Moreover, what uses as husks the copolymer obtained, combining variously the monomer used for each above-mentioned polymer can be used. Moreover, these resins may be the empty capsids which form multilayer structure. The empty capsid which uses these thermoplastic resin as husks is not limited by the manufacture technique.

[0011] Also of these empty capsids, since the hollow polymer grain in which the polystyrene system polymer / poly (meta) acrylic-ester system polymer forms multilayer structure can obtain a high voids, it is desirable.

[0012] The hollow polymer grain which can be used suitable for this invention can be manufactured according to the technique indicated by JP,64-1704,A, JP,5-279409,A, JP,6-248012,A, JP,10-110018,A, etc., using an acidic-group inclusion monomer and the monomer in which this and copolymerization are possible.

[0013] Although especially the voids (proportion of the opening section capacity of the interior to a total grain volume) of the empty capsid used for this invention is not limited, it is desirable that it is 10% or more. Furthermore, it is 30% or more preferably. If a voids is too low, gloss and the blister-proof nature enhancement effect will become inadequate. Although it is thought that the above-mentioned enhancement effect becomes large so that a voids is large, the manufacture of 90% or more of an empty capsid is difficult the voids in practice.

[0014] Although not limited especially, also as for the size of an empty capsid, it is desirable that a grain outer diameter is 0.1 micrometers or more, and its thing 0.4 micrometers or more is still desirable. As for a thing 0.1 micrometers or less, the effect of the enhancement of a coated paper besides the parvus in surface gloss also becomes [ a grain outer diameter / the blister-proof nature enhancement effect ] small.

[0015] The bowl type polymer grain which can be used for this invention has the following

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configurations. That is, the bowl type polymer grain said by this invention has the bowl type configuration [ like ] which judges a part of true sphere-like hollow polymer grain at a flat surface mostly, and is acquired where \*\* also has a void (centrum) in a core part, it is perpendicular to the decision side, and the cross section passing through the center of the original spherical hollow polymer grain is making the configuration which cut off a part of double circle by straight-line m, as shown in drawing 1. In the cross section shown in drawing 1, maximum Hmax of length H of the perpendicular from the arbitrary points on outside radii to the above-mentioned straight-line m is equal to radius  $D/2$  of circle p of the outside of the above-mentioned double circle, or depends and is large. If it puts in another way, the outer diameter of bowl type polymer grain is larger than the half (semi-sphere) of the original spherical hollow polymer grain almost, and is carrying out the interval-configuration of a semi-sphere and a spherical particle. That is, it is larger than 1, and is equal to 2, or the ratio of outer-diameter D of bowl type polymer grain and height Hmax is the parvus from 2.

[0016] The thick section of bowl type polymer grain is huge a little toward the inner direction in the neighborhood of the opening edge of a bowl. Moreover, the thick section of bowl type polymer grain may be a dense thing which may have the void (centrum) crushed in the shape of [ which originates in the interior at the void of the core part of the original hollow polymer grain ] flat, or does not have a centrum.

[0017] In this invention, an average of a mean diameter at the maximum equator (the greatest thing is said among the distance for two arbitrary points of the superficies of bowl type polymer grain.), i.e., the maximum outer diameter, uses preferably 0.3-5 micrometers of 0.5-3-micrometer bowl type polymer grain. When a mean diameter at the maximum equator is less than 0.3 micrometers, the blank paper gloss, the whiteness degree, the opacity, the printing gloss, and stiffness of a coated paper are inferior. Moreover, the bowl type polymer grain exceeding 5 micrometers cannot obtain this stably.

[0018] Moreover, the proportion of the average diameter (outer diameter containing the thick section) of opening to the mean diameter at the maximum equator of bowl type polymer grain is usually 60 - 100% preferably 25 to 100%. moreover, the mean thickness (average wall thickness) of bowl type polymer grain -- 1- of a mean diameter at the maximum equator -- it is 3 - 20% still preferably two to 50% preferably 90% Here, the mean thickness of grain means an average of the thickness of grain. Moreover, the thickness of grain means the distance of the segment formed of two intersections of the half-line and bowl type polymer grain which use the virtual center of bowl type polymer grain, i.e., the center of the precursor grain of the concerned bowl type polymer grain, as an end in the cross section shown in drawing 1. However, when the virtual center of bowl type polymer grain is situated in the interior of the thick section of bowl type polymer grain (all in the case of being in a void fraction are included when a virtual center is in the dense fraction of bowl type polymer grain), the thickness of grain means the distance of the segment from which the straight line passing through a virtual center is cut out by two intersections with the outer surface of bowl type polymer grain.

[0019] The bowl type polymer grain which has the above-mentioned characteristic feature is polymer grain which has a new configuration, and these people propose it by Japanese Patent Application No. 39834 [ nine to ]. This bowl type polymer grain can be obtained by drying, after carrying out base processing of the multilayer-structure polymer which contains an acidic group as follows, for example and carrying out acid treatment by request subsequently. In addition, in a manufacture of bowl type polymer grain, an emulsion-polymerization method is usually adopted.

[0020] Moreover, the monomers used in a manufacture of bowl type polymer grain are as follows. It is the monomer which has the functional group which indicates acidity to be an acidic-group inclusion monomer, and sulfonic group inclusion monomers, such as carboxyl group inclusion monomers, such as partial ester of unsaturated multiple-valued carboxylic acids, such as ethylene nature unsaturated carboxylic acids, such as an acrylic acid, a methacrylic acid, a cinnamic acid, an itaconic acid, a fumaric acid, and a maleic acid, an itaconic-acid monochrome ethyl, fumaric-acid monobutyl, and maleic-acid monobutyl, and a styrene sulfonic acid, etc. can be mentioned as the example. These acidic-group inclusion monomers are independent, respectively, or can be used combining two or more sorts. The monoester of a monovalent carboxylic acid and a bivalent carboxylic acid is preferably used also in an

acidic-group inclusion monomer. A methacrylic acid is the most desirable also of these.

[0021] moreover, as an acidic-group inclusion monomer and a monomer which can be copolymerized. For example, aromatic vinyl monomer; methyl (meta) acrylate, such as styrene, an alpha methyl styrene, and p-methyl styrene, Ethyl (meta) acrylate, butyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, Lauryl (meta) acrylate, glycidyl (meta) acrylate, Acrylic-ester (meta); (meta) acrylamides, such as 2-hydroxy ethyl (meta) acrylate, Acrylamides (meta), such as N-methylol (meta) acrylamide, and the derivative; butadiene of those, Halogenation vinylidene; vinylpyridines [ , such as conjugated-diene monomer; vinyl acetate, /, such as a carboxylic-acid vinyl-ester; vinyl chloride, /, such as a halogenation vinyl; vinylidene chloride, ], such as an isoprene, etc. can be mentioned. These monomers are independent, respectively or can be used combining two or more sorts. Also of these monomers, an acrylic ester (meta) and an aromatic vinyl monomer are desirable, and styrene is desirable of an aromatic vinyl monomer.

[0022] Furthermore, for example, cross-linking monomers, such as a divinylbenzene, a diallyl phthalate, allyl-compound (meta) acrylate, and ethylene \*\*\*\*\* (meta) acrylate, can be used if needed.

[0023] The formation nucleus polymer of a nucleus polymer carries out copolymerization of the monomer mixture with 70 - 45 % of the weight preferably 30 - 65 % of the weight of acidic-group inclusion monomers, and 70 - 35 % of the weight of the monomers in which it is desirable and 30 - 55 % of the weight and this, and copolymerization are possible, and is obtained. Moreover, it is desirable to perform formation of a nucleus polymer to the bottom of presence of a seed polymer, and it becomes easy to control the particle diameter of the nucleus polymer which this generates. A polymerization invert ratio is usually 97 % of the weight or more preferably 90% of the weight or more.

[0024] Under presence of a nucleus polymer, the formation heart polymer of a heart polymer carries out copolymerization of the monomer mixture with 85 - 65 % of the weight preferably 10 - 35 % of the weight of acidic-group inclusion monomers, and 90 - 65 % of the weight of the monomers in which it is desirable and 15 - 35 % of the weight and this, and copolymerization are possible, and is obtained. As occasion demands, a little cross-linking monomer can be used. or [ however, / that the inclusion proportion of the acidic-group inclusion monomer in heart polymer grain is equal to the inclusion proportion of the acidic-group inclusion monomer in nucleus polymer grain here ] -- or it considers as the parvus more the weight proportion of a nucleus polymer and a heart polymer -- the heart polymer 100 weight section -- receiving -- a nucleus polymer -- 1 - 25 weight section -- the monomer for heart polymer formation is used so that it may become 3 - 20 weight section preferably 150-550nm of the particle size of the polymer grain formed to the heart is 200-400nm still preferably preferably.

[0025] Under presence of the polymer grain formed to \*\*\*\*, 1 - 12 % of the weight of acidic-group inclusion monomers, preferably, copolymerization of 97 - 91% of the weight of the monomer mixture is carried out still preferably 98 to 90% of the weight preferably 99 - 88 % of the weight of the monomers in which it is still desirable and 3 - 9 % of the weight and this, and copolymerization are possible, and the formation interlayer polymer of an interlayer polymer is obtained two to 10% of the weight. the weight proportion of a \*\*\*\* polymer and an interlayer polymer -- usually -- 5 / 95 - 60/40 -- it is 10 / 90 - 50/50 preferably moreover, the weight proportion (polymer to the polymer/interlayer to \*\*\*\*) of the polymer formed to \*\*\*\*, and the polymer which even the interlayer formed -- usually -- it is 0.17 or more still preferably 0.1 or more preferably 0.05 or more 300-900nm of the particle size of the polymer grain which even the interlayer formed is 350-800nm still preferably preferably.

[0026] The outer-layer polymer which wraps in this substantially is formed in the periphery of the polymer grain which consists of the formation nucleus / the heart / an interlayer of an outer-layer polymer. An outer-layer polymer is formed in the bottom of presence of the polymer grain in which even the interlayer was formed the monomer which consists of 99.5 % of the weight or more of aromatic vinyl monomers, and 0.5 or less % of the weight of acidic-group inclusion monomers, and by being independent and carrying out the polymerization of the aromatic vinyl monomer preferably. As for the weight proportion (polymer to the polymer/outer layer to an interlayer) of the polymer which even the interlayer formed, and the polymer formed to the outer layer, it is desirable that it is 0.4 or more and 0.6 or less. the weight proportion (polymer to the polymer/outer layer to \*\*\*\*) with the polymer grain

formed to the polymer grain formed to \*\*\*\*, and the outer layer -- usually -- it is 0.07 or more still preferably 0.04 or more preferably 0.02 or more

[0027] At least one void (centrum) is formed into polymer grain by adding a base in aqueous variance liquid, such as a latex containing the polymer grain which has at least 4 layer structures which consist of a base processing nucleus polymer, a heart polymer, an interlayer polymer, and an outer-layer polymer, and making pH of aqueous variance liquid or more into seven (however, the void is full of the aqueous medium which forms aqueous variance liquid). As an example of the base used, ammonium-carbonate (pile) salts [, such as a carbonate (pile); ammonium carbonate of alkali metal, such as a hydroxide; sodium carbonate of alkaline earth metal, such as a hydroxide; calcium hydroxide of alkali metal, such as a sodium hydroxide, a potassium hydroxide, and a lithium hydroxide, and a magnesium hydroxide, and a potassium bicarbonate, and an ammonium bicarbonate ]; etc. can be mentioned. Also of these, the hydroxide of alkali metal is desirable. The amount of the base to use is an amount which makes seven or more pH of the aqueous variance liquid which neutralizes a part of acidic group [ at least ] in the above-mentioned polymer grain, and contains polymer grain. In order to add a base in aqueous variance liquid and to neutralize the acidic group inside polymer grain, time to spread a base inside polymer grain is required, therefore after adding a base, it is desirable to fully stir by spending time. More than the temperature of the processing temperature in base processing that is fully softened and deals in polymer grain is desirable. The processing time after base addition is usually about 15 - 120 minutes. Although the stability of aqueous variance liquid may fall by addition of a base, in order to prevent this, before adding a base, it is independent, or an anionic surface active agent and a nonionic surface active agent may be used together, and you may add. In a base down stream processing, it is not desirable to make an organic solvent which is taught to JP,3-26724,A exist. If an organic solvent, especially non-polymerization nature aliphatic hydrocarbon, etc. are made to exist, the configuration of the grain finally obtained will become not a bowl type but flat. You may make a polymerization nature monomer exist at the time of base processing. As a monomer, the monomer which does not contain an acidic group is usually used. 100 weight section of all the monomers taught when the amount manufactured the above-mentioned polymer grain -- receiving -- usually -- 1 - 20 weight section -- it is 2 - 10 weight section preferably

[0028] The polymer aqueous variance liquid which carried out acid-treatment base processing can be processed from an acid, if it is a request, and the pH can be made less than into seven. Thereby, a particle diameter and the diameter of a void can be enlarged. Especially the acid used here is not limited but can mention organic acids, such as mineral-acid; acetic acids, such as a hydrochloric acid and a sulfuric acid, and a malonic acid, as the example. Moreover, an acidic-group inclusion monomer can be used. total section of monomer 100 weight used for synthesis of a nucleus polymer, a heart polymer, an interlayer polymer, and an outer-layer polymer when an acidic-group inclusion monomer was used -- receiving -- usually -- 0.01 - 40 weight section -- desirable -- 0.05 - 20 weight section -- it is used in the domain of 0.2 - 10 weight section still preferably Moreover, you may make the monomer in which this and copolymerization are possible live together with an acidic-group inclusion monomer in an acid-treatment process. In this case, these monomers constitute a part of monomer for the outermost layer polymer formation mentioned later. an acidic-group inclusion monomer -- total section of monomer 100 weight for outermost layers -- receiving -- usually -- 0.1 - 20 weight section -- it is preferably used in the domain of 0.5 - 10 weight section Processing temperature, the processing time, etc. in an acid-treatment process are the same as that of the conditions of base processing almost. Although the stability of aqueous variance liquid may fall by addition of an acid, in order to prevent this, before adding an acid, it is independent, or an anionic surface active agent and a nonionic surface active agent may be used together, and you may add.

[0029] After formation base processing of an outermost layer polymer, or after performing acid treatment further, an outermost layer polymer can be formed in the periphery of an outer-layer polymer by request by being independent about an aromatic vinyl monomer, or carrying out the polymerization of 90 % of the weight or more of aromatic vinyl monomers, the monomer in which this and copolymerization are possible, and the monomer mixture which consists of 10 or less % of the weight of



acidic-group inclusion monomers preferably to the bottom of present polymer grain. In addition, an acidic-group inclusion monomer can be added at the process of acid treatment as mentioned above. the weight proportion (the polymer / outermost layer polymer to an outer-layer polymer) of the polymer grain and the outermost layer polymer which were formed to the outer-layer polymer -- usually -- 100 / 10 - 50/100 -- it is 100 / 25 - 100/100 preferably By request, the cross-linking monomer of a few rate can be used as a part of monomer for outermost layer polymer formation.

[0030] xeransis -- the hollow polymer grain which has at least one void as mentioned above in the phase which ended the base down stream processing is formed However, in this phase, the void in polymer grain is full of the aquosity medium. By drying the aquosity variance liquid of this polymer grain, the polymer grain which has a bowl type configuration can be obtained. While an internal aquosity medium vaporizes in connection with advance of xeransis, it caves in so that the coat of hollow polymer grain may be turned up inside, and it is thought that the whole grain becomes a bowl type configuration. That is, in connection with advance of xeransis, the amount of [ increase and ] centrum becomes small gradually, and, finally the degree of a collapse serves as the bowl type polymer grain the amount of [ the parvus for a centrum or ] centrum is not. Xeransis is dried according to a conventional method, after carrying out the direct drying of the aquosity variance liquid by technique, such as a spray drying, or solidifying by the usual latex solidifying method and separating hollow polymer grain. The bowl type polymer grain the amount of centrum is not (it is dense) can be obtained by drying comparatively quickly. According to the spray drying, the bowl type polymer grain the amount of centrum is not (it is dense) can be obtained directly.

[0031] The multilayer coated paper of this invention is obtained by forming the top layer which comes to contain an empty capsid or bowl type polymer grain, a pigment, and adhesives on the coating layer (it being hereafter called an interlayer) formed on the coating layer (it may be hereafter called an undershirt layer) which carried out the direct coating to stencil paper, or the undershirt layer. Formation of a top layer is performed by applying the constituent for top layer coatings which comes to contain an empty capsid or bowl type polymer grain, a pigment, and adhesives on an undershirt layer or an interlayer. Moreover, a top layer can be formed on an undershirt layer or an interlayer also by applying the constituent for top layer coatings which comes to contain the aquosity variance liquid, the pigment, and adhesives of the polymer grain (it may be hereafter called "precursor grain") which gives bowl type polymer grain at the time of xeransis.

[0032] Although the device in which blister-proof nature etc. is improved by preparing the coating layer which contains an empty capsid as a top layer is not clear, in a printing xeransis process, an empty capsid deforms under an elevated temperature, \*\*\*\*\* is formed, and it is surmised whether steam permeability is raised.

[0033] Moreover, when using bowl type grain, \*\*\*\*\* to which the air permeability of a coated paper already originates in the configuration of bowl type grain judging from a high thing at the time of the coating stratification is formed, and it is surmised that it is a thing with high steam permeability for this reason.

[0034] As adhesives used for the constituent for coatings for the top stratification, there is especially no limit and what is used for the paper coating can be used conventionally. As an example of such adhesives, gelatin, casein, a starch derivative, Polyvinyl alcohol, denaturation polyvinyl alcohol, a hydroxy cellulose, A methyl cellulose, a carboxymethyl cellulose, polyvinyl acetate, Polyurethane, an ethylene-acrylic-acid alkali-salt copolymer, an ethylene-maleic-anhydride alkali-salt copolymer, An ethylene-vinyl acetate copolymer, a styrene-maleic-acid copolymer, a styrene-butadiene system copolymer, Adhesives or a latex of the nature like a copolymer grade or synthesis etc. is mentioned acrylic-ester resin, acrylic-ester-vinyl acetate copolymer, and acrylic-acid amide-acrylic-ester-vinyl acetate of 3 yuan. These adhesives can also be used combining two or more kinds if needed.

[0035] In this invention, a styrene-butadiene system copolymer latex and the copolymer latex which carries out copolymerization of the monomer which can be copolymerized to these, and is obtained especially carboxy denaturation styrene-butadiene system copolymer latex, division, conjugated-diene monomer, aromatic vinyl monomer, alpha, and beta-unsaturated-carboxylic-acid monomer and if needed



are suitably used among the above-mentioned adhesives.

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